

FORM PTO-1390 (Modified)  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

1247-0796-0V PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

**09/147813**INTERNATIONAL APPLICATION NO.  
**PCT/FR98/01513**INTERNATIONAL FILING DATE  
**10 JULY 1998**PRIORITY DATE CLAIMED  
**15 JULY 1997**

## TITLE OF INVENTION

**PLASTIC WINDOW, ESPECIALLY FOR MOTOR VEHICLES, AND PROCESS FOR ITS MANUFACTURE**

## APPLICANT(S) FOR DO/EO/US

**Jean-Louis BRAVET, et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 18 below concern document(s) or information included:**

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

**Request for Consideration of Documents Cited in International Search Report****Notice of Priority****PCT/IB/304****PCT/IB308**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

PCT/FR98/01513

1247-0796-0V PCT

20. The following fees are submitted:

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :**

- ☒ Search Report has been prepared by the EPO or JPO ..... **\$840.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... **\$670.00**
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... **\$760.00**
- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$970.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... **\$96.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$840.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than ☒ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).**\$130.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	- 20 =	0	x \$18.00
Independent claims	- 3 =	0	x \$78.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>

**\$0.00****\$0.00****\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$970.00**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐**\$0.00****SUBTOTAL =****\$970.00**Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). ☐**\$0.00****TOTAL NATIONAL FEE =****\$970.00**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐**\$0.00****TOTAL FEES ENCLOSED =****\$970.00**

Amount to be:

refunded

\$

charged

\$

☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C.**  
1755 Jefferson Davis Highway, Fourth Floor  
Crystal Square Five  
Arlington, Virginia 22202  
703-413-3000

**William E. Beaumont****Registration Number 30,996**

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

**March 12, 1999**

1247-0796-0V PCT

#5/a

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :  
JEAN-LOUIS BRAVET ET AL : ATTN: NEW APPLICATION DIVISION  
SERIAL NO: 09/147,813 :  
FILED: MARCH 12, 1999 :  
FOR: PLASTIC WINDOW, ESPECIALLY:  
FOR MOTOR VEHICLES, AND  
PROCESS FOR ITS  
MANUFACTURE

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend this case as follows:

IN THE SPECIFICATION

Page 1, at the top of the page, insert:

--TITLE OF THE INVENTION--;

above line 4, insert:

--BACKGROUND OF THE INVENTION

Field of the Invention--;

above line 11, insert:

--Description of the Background--.

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Page 3, at the top of the page, insert:

--SUMMARY OF THE INVENTION--;

after line 22, insert:

--DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

#### IN THE CLAIMS

Please cancel Claims 1-17 without prejudice, and insert the following new claims:

--18. A product, which is at least partly transparent and of optical quality equivalent to that of a window, which comprises a plastic core coated with a skin comprising at least one plastic film supporting a scratch-resistant layer.

19. The product of Claim 18, wherein said skin has a thickness of at most equal to 500  $\mu\text{m}$ , and comprises of one or more transparent thermoformable plastic films made of polycarbonate, polypropylene, poly(methyl methacrylate) an ethylene/vinyl acetate copolymer, poly(ethylene terephthalate), polyurethane, polyvinyl butyral or a cycloolefin copolymer, between which is interposed, or on which is deposited, at least one functional layer, wherein at least one of said thermoformable plastic films optionally constitutes one of said functional layers.

20. The product of Claim 19, wherein the scratch-resistant layer has a thickness of between 1 and 10  $\mu\text{m}$ , and the scratch-resistant layer is inorganic, or consists essentially of networks of entangled inorganic and organic molecular chains linked to each other by silicon-carbon bonds.

21. The product of Claim 20, wherein said inorganic scratch-resistant layer consists essentially of polysiloxanes, silica or alumina.

22. The product of Claim 19, wherein the skin has an external surface which is hydrophobic/oleophobic and wherein an external layer of which the skin is composed comprises a hydrophobic/oleophobic agent, said external layer comprising said scratch-resistant layer, wherein said hydrophobic/oleophobic agent is incorporated, or of a thin layer, having a thickness of between 2 and 50 nm, consisting essentially of the said hydrophobic/oleophobic agent, said thin layer being obtained by grafting, or a layer of the said hydrophobic/oleophobic agent, said layer being supported on a film of poly(vinyl fluoride) or poly(vinylidene fluoride).

23. The product of Claim 22, wherein said hydrophobic agent is a fluorinated polysilane.

24. The product of Claim 18, wherein said skin includes at least one decorative or masking layer or both covering all or part of the surface of the product, said layer being positioned directly under the film supporting the scratch-resistant layer.

25. The product of Claim 18, wherein said skin includes at least one adhesion layer constituting the internal surface of the skin intended to come directly into contact with the core of the product.

26. The product of Claim 18, wherein the skin includes one or more optically selective layers, having thicknesses of between 2 and 35 nm and separated from each other, as well as from other adjacent layers or films, by dielectric layers.

27. The product of Claim 25, wherein said optically selective layers are metal layers.

28. The product of Claim 18, wherein said core comprises of a thermoplastic, comprising polycarbonate, poly(methylmethacrylate), an ethylene/vinyl acetate copolymer, poly(ethylene terephthalate), polyurethane or a cycloolefin copolymer, or an ionomer resin or

a thermosetting or thermally crosslinkable material of the polyurethane, unsaturated polyester, ethylene/vinyl acetate copolymer, or a combination of several thicknesses of the same one or several of these plastics, wherein the core thus formed is chemically compatible with the said skin and is capable of giving the assembly the required mechanical properties.

29. The product of Claim 18, which is bent and in that it forms a motor-vehicle window having, in particular, the regulation optical properties.

30. The product of Claim 18, wherein the scratch-resistant layer has a surface appearance without any crazing.

31. A process for manufacturing the product of Claim 18, which comprises:

a) first, in assembling constituent elements of a skin by laying them approximately flat, or by supplying them from a device of developable shape, and optionally, subjecting the constituent elements of the skin to consolidation, then,

b) secondly, subjecting the skin to heat treatment, the skin being supported completely or partly by a mould surface, an auxiliary means for shaping at least part of the skin to the said mould surface, being optionally provided so as to relax stresses in the skin, and crosslinking certain constituent elements thereof; and

c) third, in joining the skin to a plastic core by hot pressing in a form, or by thermoplastic injection moulding or reactive injection moulding of the material of the core, the skin having been positioned in the bottom of the mould in such a way that its constituent scratch-resistant layer and/or hydrophobic/oleophobic layer is in direct contact with the mould.

32. The process of Claim 31, wherein said constituent elements are supplied by screen printing, flexography, ink-jet printing, laser printing, dip coating or spraying.

33. The process of Claim 31, wherein in step b), said heat treatment is effected at 100° to 300°C.

34. A process for manufacturing the product of Claim 18, which comprises:

a) depositing the constituent elements of a scratch-resistant layer on a substantially flat plastic film; and

b) shaping said film bearing the elements of the scratch-resistant layer into a shape which is the same as or at least similar to the ultimate shape of the end-product, at least in certain parts, while at the same time at least partly crosslinking this scratch-resistant layer.

35. The process of Claim 31, wherein the crosslinking and simultaneous shaping involve a heat treatment at a temperature of between 100 and 300°C, and more precisely between 140 and 240°C.

36. The process of Claim 34, wherein the shaping is carried out by supporting the film coated with the scratch-resistant layer, or the elements intended to constitute this layer, at least on part of its surface, by a mould.

37. The process of Claim 36, wherein the mould carrying the film is a frame open at its center.

38. The process of Claim 34, wherein the film coated with the scratch-resistant layer of elements constituting this layer is combined, before shaping, with one or more other films which themselves fulfill functions or carry means, such as screen-printed decorations or layers, carrying out these functions other than the scratch-resistance function.

39. A method of incorporating a body element, at least a portion of which is transparent, in a manufactured object, which comprises incorporating the product of Claim 18 into said manufactured object.--

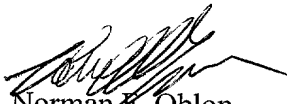
REMARKS

Claims 1-17 have been cancelled. New Claims 18-39 have been added. Claims 18-39 are now active in this case.

All of the above amendments are fully supported by the claims and disclosure as originally filed. No new matter has been added. The specification has been amended to include appropriate headings.

Accordingly, it is believed that the present application is now in condition for examination on the merits. Favorable consideration is earnestly solicited.

Respectfully submitted,  
OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.

  
Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

William E. Beaumont  
Registration No. 30,996  
~~Robert F. Gnuse~~  
**Registration Number 27,295**

Crystal Square Five - Fourth Floor  
1755 Jefferson Davis Highway  
Arlington, VA 22202  
(703) 413-3000  
Fax #: (703) 413-2220  
NFO/WEB:jlf

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**PLASTIC WINDOW, ESPECIALLY FOR MOTOR VEHICLES, AND  
PROCESS FOR ITS MANUFACTURE**

5 The present invention relates to at least  
partly transparent products made of plastic, especially  
products of high optical quality, equivalent to that of  
a glass window. It is conceivable to replace glass  
sheets with plastic sheets in the construction of  
windows, for example for buildings or transport  
10 vehicles.

Compared with glass, plastics are lower in  
weight, which is a key advantage in the case of  
electrically driven town vehicles, in so far as an  
increase in their range is crucial. In such vehicles,  
15 it could even be envisaged producing, from plastic, in  
a single unit, entire doors or even complete sides of  
the body, including the windows, and, optionally,  
painting a lower part thereof. In general, the low  
weight of the transparent surfaces is relatively  
20 advantageous in the case of modern transport vehicles  
in so far as technical progress is going hand in hand  
with integration into windows of still more numerous  
functions (heated rear window, radio antenna,  
windscreen de-icing, colouration in order to prevent  
25 the passenger compartment heating up in strong  
sunlight, incorporation of electrochromic compounds,  
display of information on the windscreen, etc.) and  
with ever increasing amounts of glazed surfaces. This  
results in a general increase in the vehicle weight, to  
30 the detriment of its energy consumption.

Moreover, compared with glass, plastics are  
capable of providing improved safety conditions and  
superior anti-theft protection because of their greater  
toughness.

35 A not insignificant advantage of plastics  
compared with glass resides in their superior ability  
to be easily converted into complex shapes.

Finally, the ability of plastic sheets to be  
deformed substantially reversibly makes it possible to

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envisage ways of fitting them into considerably simplified body openings by a snap-fastening mechanism, from the inside just as from the outside of the vehicle.

5           According to a first approach, flat plastic sheets are formed by extrusion, a component is cut to the required dimensions and fastened to a thermoforming device, a contact thermoforming operation is carried out with at least one solid mould surface and,  
10 optionally, with the aid of compressed air or suction. The optical properties of a sheet thus extruded are not satisfactory.

Furthermore, the scratchability of plastics, mentioned previously, is such that, in their optical  
15 applications or as transparent elements, it is necessary to coat the shaped components with a hard varnish. This operation is accompanied, as is well known to those skilled in the art, by problems of the varnish flaking, these problems being more acute in the  
20 case of surfaces of complex shapes. In addition, it has only been envisaged forming the hard varnish at a temperature below the deformation temperature or softening point of the plastic, the shape of which is thus entirely preserved during this operation. Such  
25 conditions of forming the varnish are excessively restrictive and have resulted in considerable effort being expended to produce varnishes which form at sufficiently low temperatures and, at the same time, thermoplastics with high softening points. There  
30 therefore remained the need for a plastic which is transparent or intended for optical applications, in which the poor optical quality inherent in the extrusion technique and the problem of the varnish flaking would be avoided and in which many varnishes  
35 could be employed in combination with many plastics under satisfactory compatability conditions.

This product should be capable of being obtained by an inexpensive, reliable and simple process.

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These objectives are presently achieved by the invention, the subject of which is a product which is at least partly transparent and of high optical quality. More particularly, the invention resides in the fact that this product comprises a plastic core integral with a skin comprising at least one plastic film supporting a scratch-resistant layer.

This is because the property by which the scratch-resistant layer is supported on a plastic film guarantees easy and reliable procurement of an end-product of lasting high optical quality, as will become apparent in the rest of the description. It makes it possible to produce such an end-product on the basis of the scratch-resistant layer on its support film in a physical and chemical state which will not be modified consequently, or only very slightly, by combining it with the core especially by injection moulding the plastic of which it is composed. The use of certain scratch-resistant varnishes forming at relatively high temperatures optionally requires choosing a material for the support film which is sophisticated but in a low quantity.

The expression "high optical quality or optical quality equivalent to that of a window" is understood to mean, in the sense of the invention, "optical quality equivalent to that of a glass window, which can be approved as a motor-vehicle window according to the various standards in force, especially the R 43 standard in use in France".

Whatever the material of the core, the injection-moulding temperatures should not, of course, affect the other constituents of the product. This material may be chosen from many plastics; it may be a conventional inexpensive thermoplastic having a relatively low softening point. According to the invention, the plastic of the core is capable of interacting with the skin for the purpose of obtaining high optical quality, while at the same time having the

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desired mechanical properties, in particular flexural strength and impact strength.

Preferably, the skin has a thickness at most equal to 500  $\mu\text{m}$ , particularly preferably between 10 and 100  $\mu\text{m}$ , and comprises one or more transparent thermoformable plastic films, for example made of polycarbonate (PC), polypropylene (PP), poly(methyl methacrylate) (PMMA), an ethylene/vinyl acetate copolymer (EVA), poly(ethylene terephthalate) (PET), polyurethane (PU), polyvinyl butyral (PVB) or a cycloolefin copolymer (COC), i.e. an ethylene/norbornene copolymer or an ethylene/cyclopentadiene copolymer. One or more functions may be assigned to some of these thermoformable plastic films by the incorporation of suitable agents. Depending on its thickness and its nature, the skin is capable of contributing to a greater or lesser extent to the mechanical properties of the product.

Moreover, a functional layer may be deposited on a thermoformable plastic film of the skin, this being, in particular, the case with the scratch-resistant layer. Finally, a functional layer may be sandwiched, autonomously, between two thermoformable plastic films.

Advantageously, the scratch-resistant layer has a thickness of between 1 and 10  $\mu\text{m}$ ; generally, it forms the external surface of the product of the invention. It may essentially be inorganic and especially consist of polysiloxanes and/or of derivatives of silica and/or alumina, or a hybrid, such as consisting of networks of entangled inorganic and organic molecular chains linked to each other by means of silicon-carbon bonds. Such a hybrid layer exhibits excellent transparency, adhesion and scratch-resistance properties. It appears that the inorganic network gives the coating its hardness and its scratch resistance while the organic network gives it its elasticity and its toughness. Such varnishes are well known and have been described in the published applications EP-A1-0,524,417 and EP-A1-0,718,348, the

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teaching of which is incorporated here by way of reference; some of these varnishes are especially denoted by the registered trademark "Ormocer" which is an abbreviation for "Organically Modified Ceramic". It is worth pointing out that the firing temperature of Ormocers is easily adaptable by varying the relative amounts of the organic polymer fraction and the inorganic fraction. With regard to the plastic of the support film, it may be useful, or indeed necessary, to adapt its composition so as to make it compatible with the method and temperature of deposition of the scratch-resistant layer.

Other functionalities may be incorporated into the skin.

According to one particular embodiment, the external layer of the skin, in contact with the environment, contains a hydrophobic/oleophobic agent which therefore imparts this property to the external surface of the product. As hydrophobic/oleophobic agent, fluorinated polysilanes are well known, especially those obtained from precursors having a hydrolysable alkoxy- or halogeno- type functional group at one end, this functional group serving for chemical bonding to the substrate, and a perfluorinated carbon chain at the other end, this chain being intended to constitute the external surface of the product.

The hydrophobic/oleophobic agent is, in decreasing order of preference, incorporated into the scratch-resistant layer, which has a chemical structure close to its own, or with which it is at the very least chemically compatible, or grafted in the form of a thin layer having a thickness of between 2 and 50 nm, preferably onto the scratch-resistant layer, or alternatively self-supported on a plastic film, such as a poly(vinyl fluoride) (PVF) or a poly(vinylidene fluoride) (PVDF), to be advantageously applied directly to the scratch-resistant layer.

According to a variant, at least one decorative and/or masking layer, covering all or part of the

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surface of the product, is positioned in the skin, preferably directly under the support film of the scratch-resistant layer.

5 This layer may, for example, replace the screen-printed decoration often deposited around the periphery of the internal face of windows, especially for motor vehicles, for the purpose of masking, in the case of an observer outside the vehicle, the body elements forming the frame of the opening and the  
10 adhesive bead which is thus protected from degradation by ultraviolet radiation. This layer may include opaque or transparent coloured decorative elements, making it possible to produce coloured elements matching the body or the internal fittings, logos, etc.

15 The skin may be provided with an adhesion layer, in particular on its internal face for fastening to the core, but also between two films or layers of the skin. Standard adhesives are polyvinyl butyral or polyurethane.

20 Finally, among the main constituents of the skin are the optically selective layers which are stacked, for example beneath the decorative and/or masking layer. These layers are distinguished by a high transmission in the visible range (wavelengths from 400  
25 to 800 nm) and a high absorption and/or reflection in the ultraviolet range ( $< 400$  nm) and infrared range ( $> 800$  nm). These layers may consist of thin metal layers, for example based on silver, having thicknesses of between 2 and 35 nm, separated from each other, as  
30 well as from other adjacent layers or films, by dielectric layers of oxides or nitrides of indium, tin, silicon, zinc, titanium, tungsten, tantalum, niobium, aluminium, zirconium, etc., generally having thicknesses of between 10 and 150 nm. These layers may  
35 include at least one bulk-coloured layer.

The combination of these layers may be electrically conductive; it may belong to the family of solar-protection stacks used for limiting the influx of heat by solar radiation into closed spaces or to that

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of low-emissivity stacks used, on the contrary, to limit the loss of heat from closed spaces, this loss being mainly due to transmission of infrared radiation through the window. Such stacks are described in  
5 Patents FR 2,708,926 and EP 0,678,484.

The core of the product of the invention consists of a thermoplastic such as polycarbonate, poly(methyl methacrylate), an ethylene/vinyl acetate copolymer, poly(ethylene terephthalate), a cycloolefin  
10 copolymer (for example, an ethylene/norbornene or ethylene/cyclopentadiene copolymer), or of an ionomer resin (an ethylene/methacrylic acid copolymer or an ethylene/acrylic acid copolymer neutralized with a polyamine, etc.), or of a thermosetting or thermally  
15 crosslinkable material (polyurethane, unsaturated polyester, ethylene/vinyl acetate copolymer), or else of a combination of several thicknesses of the same one or several of these plastics, on condition that the core is chemically compatible with the skin of the  
20 product according to the invention and gives the assembly the required mechanical properties.

The subject of the invention is also a process for manufacturing the product described above.

In a first phase of this process, the  
25 constituents of the skin are assembled, this being in the form of a ply or developed, optionally plane.

The scratch-resistant layer, when it is made of polysiloxanes, is advantageously formed cold on its support film and/or by plasma-enhanced deposition, such  
30 as plasma CVD (Chemical Vapour Deposition). Insofar as polysiloxanes formed in this way are no longer reactive, having already completely reacted, it is necessary to choose the composition of the scratch-resistant layer so that it can be bent, in order to  
35 avoid subsequent flaking problems.

When the scratch-resistant layer consists of Ormocers, these are applied flat in the form of liquid precursors to the support film, using the conventional techniques of flow coating, dip coating, especially in

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a bath of small volume for the sake of economizing, liquid spraying or curtain spraying. The precursor consists, for example, of colloidal dispersions in solvents of several hybrid compounds, that is to say compounds which are both organic and inorganic, or of low-molecular-weight polymers functionalized by SiOR groups in a mixture with tetraethoxysilane. The scratch-resistant layer is then cured using a sol-gel process in which the precursor is firstly dried, passing through the intermediate state of a gel, by moderate radiation or heating, especially, in the latter case, at less than 50°C. The support film is then always held substantially flat; the curing of the Ormocer is completed during the second phase of the process, described below, which consists in thermoforming the said skin by ultraviolet radiation and/or heating to temperatures of 100 to 300°C, and more specifically 140 - 240°C.

In either case, the layers, in particular the scratch-resistant layer on the assembled and bent end-product, meet the required properties for its use, especially the regulation optical properties when it is to be used as glazing or as an element comprising a window for a transport vehicle, especially a motor vehicle.

The often complex shapes of motor-vehicle windows mean that the scratch-resistant layer in particular must be able to be bent without flaking and without cracking. Thus, advantageously, the scratch-resistant layer is only fully cured after its support has been shaped and, preferably, it only starts to cure and crosslink at the same time as its support is being shaped, so as finally to have a surface appearance without crazing or flaking.

The deposition and formation techniques which have just been described may also be used for incorporating the hydrophobic/oleophobic function, whether the corresponding agent forms an integral part of the scratch-resistant layer or is supported on a

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plastic film; when it is grafted on as a thin layer, it is also preferably formed by depositing it in liquid form by spraying, if it consists of silanes, or by evaporation using techniques such as plasma CVD, optionally under vacuum.

The decorative and masking layer or layers are provided on support films, especially made of plastic, according to the techniques used in printing: screen printing, flexography, ink-jet printing, laser printing, etc.

The adhesion layer is usually provided in the form of an integral thermoplastic film.

The formation of optically selective stacks makes use of successive deposition operations using sputtering, especially sputtering assisted by a magnetic field, or the like. In this regard, reference may again be made to Patents FR 2,708,926 and EP 0,678,484.

The first phase of the process of the invention for forming the substantially flat skin may be concluded by an operation whose purpose is to consolidate the constituents thereof to a greater or lesser extent, especially by cold calendering or calendering at a temperature slightly above room temperature.

As briefly mentioned above, the second phase of the process consists in thermoforming the skin at a preferred temperature of 100 - 300°C into a shape, optionally non-developable, identical to that of the end-product.

To do this, it is advantageous, in particular in order to complete the curing and/or crosslinking of the scratch-resistant layer, to allow it to come into contact with the ambient atmosphere, that is to say without coming into contact with solid elements; only the other face of the skin is then in contact with a support whose purpose is to give it shape. Auxiliary means, for example, blowing or suction means, may be used to shape at least part of the skin to this

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support. Apart from completing the crosslinking of certain constituents, the heat treatment carried out in this second phase has the effect of relaxing the stresses in the skin.

5           The third phase of the process of the invention consists in joining the skin to a plastic core by hot pressing in a form or by thermoplastic injection moulding or reactive injection moulding (RIM) of the material of the core, the skin having been positioned  
10 in the bottom of the mould, at the start of this third phase, in such a way that its scratch-resistant layer and/or its hydrophobic/oleophobic layer, which layer is fully cured and/or crosslinked, i.e. virtually no longer reactive, is in direct contact with the mould  
15 wall.

Another object of the invention is the application of the product described above as a body element, a transparent part of which forms a window, especially for motor vehicles.

20           The invention will now be illustrated by the following example.

#### EXAMPLE

The scratch-resistant coating described in the example in Patent Application EP-A-0,718,348 is  
25 deposited as a 20 µm thick liquid film on an 80 µm thick film of standard polycarbonate prepared from bisphenol A, sold by Bayer AG under the registered trademark "Makrolon®", which has a glass transition temperature  $T_g$  equal to 145°C, by flow coating.

30           The coated support film is then placed in the bottom of a mould, the scratch-resistant layer being positioned on top; the assembly is then subjected to a heat treatment of 155°C for 30 min. A skin in the sense of the present invention is then formed, this having  
35 its virtually final shape.

The skin is placed in the bottom of an injection mould so that the scratch-resistant layer is in contact with the mould wall. There then follows, in the manner described above, the thermoplastic injection

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moulding, on two different specimens, of a 5 mm thick layer, on the one hand, and a 10 mm thick layer, on the other hand, of the same standard polycarbonate as that making up the support film of the scratch-resistant layer.

The laminate obtained exhibits a transparency and an optical quality which are amply sufficient for application as a window.

The process of the invention has the advantages inherent in the injection-moulding technique. It is thus possible to form the injection-moulded component with a peripheral bead in order to increase its stiffness, or with a relief and/or extensions, such as ribs, profiles, tabs or lugs, and/or to arrange one or more inserts, especially metal inserts, in the plastic. This arrangement is particularly useful for gripping or fastening the product of the invention, as well as for fitting it in its intended final position, such as in a body opening of a motor vehicle. In the latter case, forming suitable peripheral profiles makes it possible to envisage fitting the product from inside the vehicle, i.e. from inside the passenger compartment. The adhesive bead is then placed under the edge of the body opening and is not exposed to solar radiation. Protecting the adhesive bead with a varnish formed around the periphery of the internal face of the sheet becomes, of course, superfluous.

The appendages formed around the periphery of the product while it is being injection moulded may be preserved, or sawn off completely or partly depending on their use. After such sawing, a rubbing-down operation may be provided.

A peripheral profile with a geometry which is symmetrical with respect to the plane of the product may be opportune, for example in the case of transparent side surfaces of transport vehicles, it being possible for one or other part of the profile to be subsequently sawn off, depending on whether it is a left-hand or right-hand transparent element.

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Moreover, optional inserts may be associated with the incorporation into the product of special functions, such as a stop light in a rear window.

5 Finally, the process of the invention is economic, easy and reliable and allows the use of many combinations of constituents without the problem of their compatability, especially from the standpoint of their processing temperatures, arising.

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CLAIMS

1. Product, which is at least partly transparent and of optical quality equivalent to that of a window, characterized in that it comprises a plastic core coated with a skin comprising at least one plastic film supporting a scratch-resistant layer.

2. Product according to Claim 1, characterized in that the thickness of the skin is at most equal to 500  $\mu\text{m}$ , preferably between 10 and 100  $\mu\text{m}$ , and in that the skin consists of one or more transparent thermoformable plastic films, especially made of polycarbonate, polypropylene, poly(methyl methacrylate) an ethylene/vinyl acetate copolymer, poly(ethylene terephthalate), polyurethane, polyvinyl butyral or a cycloolefin copolymer, between which is interposed, or on which is deposited, at least one functional layer, it being possible moreover for at least one of these films itself to constitute one such functional layer.

3. Product according to Claim 1 or 2, characterized in that the thickness of the scratch-resistant layer is between 1 and 10  $\mu\text{m}$  and in that this scratch-resistant layer is essentially inorganic, especially consisting of polysiloxanes and/or based on silica and/or on alumina, or essentially consists of networks of entangled inorganic and organic molecular chains linked to each other by means of silicon-carbon bonds.

4. Product according to Claim 3, characterized in that the external surface of the skin is hydrophobic/oleophobic and in that the external layer of which the skin is composed contains a hydrophobic/oleophobic agent, especially of the fluorinated polysilane type, the said external layer consisting of the said scratch-resistant layer in which the said hydrophobic/oleophobic agent is incorporated, or of a thin layer, having a thickness of between 2 and 50 nm, essentially consisting of the said hydrophobic/oleophobic agent, such a thin layer being obtained by

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grafting, or else of a layer of the said hydrophobic/oleophobic agent, this layer being supported on a film of the poly(vinyl fluoride) or poly(vinylidene fluoride) type.

5 5. Product according to one of Claims 1 to 4, characterized in that the said skin includes at least one decorative and/or masking layer covering all or part of the surface of the product, this layer being preferably positioned directly under the film  
10 supporting the scratch-resistant layer.

6. Product according to one of Claims 1 to 5, characterized in that the said skin includes at least one adhesion layer constituting, in particular, the internal surface of the skin intended to come directly  
15 into contact with the core of the product.

7. Product according to one of Claims 1 to 6, characterized in that the said skin includes one or more optically selective layers, for example thin metal layers, especially based on silver, having thicknesses  
20 of between 2 and 35 nm and separated from each other, as well as from other adjacent layers or films, by dielectric layers.

8. Product according to one of Claims 1 to 7, characterized in that the said core consists of a  
25 thermoplastic such as polycarbonate, poly(methylmethacrylate), an ethylene/vinyl acetate copolymer, poly(ethylene terephthalate), polyurethane or a cycloolefin copolymer, or of an ionomer resin or of a thermosetting or thermally crosslinkable material  
30 of the polyurethane, unsaturated polyester, ethylene/vinyl acetate copolymer type, or else of a combination of several thicknesses of the same one or several of these plastics, given that the core thus formed is chemically compatible with the said skin and  
35 is capable of giving the assembly the required mechanical properties.

9. Product according to one of the preceding claims, characterized in that it is bent and in that it

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forms a motor-vehicle window having, in particular, the regulation optical properties.

10. Product according to one of the preceding claims, characterized in that the scratch-resistant  
5 layer finally has a surface appearance without any crazing.

11. Process for manufacturing a product according to one of Claims 1 to 10, which consists:

• firstly, in assembling the constituent  
10 elements of a skin by laying them approximately flat, or by supplying them from a device of developable shape, especially by screen printing, flexography, ink-jet printing, laser printing, dip coating or spraying, these being optionally combined with vacuum  
15 deposition techniques of the sputtering or evaporation type, and, where appropriate, in subjecting the constituent elements of the skin to an operation whose purpose is to consolidate them to a greater or lesser extent, then,

20 • secondly, in subjecting the skin to a heat treatment, preferably at a temperature of between 100 and 300°C, the skin being supported completely or partly by a mould surface, an auxiliary means for shaping at least part of the skin to the said mould  
25 surface, especially by blowing or by suction, being optionally provided so as to relax the stresses in the skin, and in crosslinking certain constituent elements thereof and

• thirdly, in joining the skin to a plastic  
30 core by hot pressing in a form, or by thermoplastic injection moulding or reactive injection moulding of the material of the core, the skin having been positioned in the bottom of the mould in such a way that its constituent scratch-resistant layer and/or  
35 hydrophobic/oleophobic layer is in direct contact with the mould.

12. Process for manufacturing a product according to one of Claims 1 to 10, comprising the steps:

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• of depositing the constituent elements of a scratch-resistant layer on a substantially flat plastic film and

5        • of shaping this film bearing the elements of the scratch-resistant layer into a shape which is the same as or at least similar to the ultimate shape of the end-product, at least in certain parts, while at the same time at least partly crosslinking this scratch-resistant layer.

10 13. Process according to Claim 12, characterized in that the crosslinking and simultaneous shaping involve a heat treatment at a temperature of between 100 and 300°C, and more precisely between 140 and 240°C.

14. Process according to either of Claims 12 and  
15 13, characterized in that the shaping is carried out by  
supporting the film coated with the scratch-resistant  
layer, or the elements intended to constitute this  
layer, at least on part of its surface, by a mould.

15. Process according to Claim 14, characterized in  
20 that the mould carrying the film is a frame open at its  
centre.

16. Process according to one of Claims 11 to 15, characterized in that the film coated with the scratch-resistant layer or elements constituting this layer is combined, before shaping, with one or more other films which themselves fulfil functions or carry means, such as screen-printed decorations or layers, carrying out these functions other than the scratch-resistance function.

30 17. Application of a product according to one of  
Claims 1 to 10 as a body element, a transparent part of  
which forms a window, especially for motor vehicles.

[illegible]



# PATENT

PLASTIC WINDOW, ESPECIALLY FOR MOTOR VEHICLES, AND  
PROCESS FOR ITS MANUFACTURE

Filed by: SAINT-GOBAIN VITRAGE

Inventors: Jean-Louis BRAVET  
Marc MAURER

## ABSTRACT

The invention relates to a product which is at least partly transparent and of high optical quality, equivalent to that of a glass window, which can be approved as a motor-vehicle window according to the various standards in force, and having a plastic core coated with a skin comprising at least one plastic film coated with a scratch-resistant layer; it also relates to a process for manufacturing this product and to the application of the latter as a body element, part of which forms a window, for example for motor vehicles.

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# Declaration, Power Of Attorney and Petition

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PLASTIC GLAZING, IN PARTICULAR FOR MOTOR CAR AND METHOD FOR

MAKING SAME (as amended)

the specification of which

☐ is attached hereto.

☒ was filed on 12 March 1999 as  
Application Serial No. 09/147,813  
and amended on \_\_\_\_\_.

☒ was filed as PCT international application  
Number PCT/FR98/01513  
on 10 July 1998,  
and was amended under PCT Article 19  
on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
<u>97/08934</u>	<u>FRANCE</u>	<u>15 July 1997</u>	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

_____ (Application Number)	_____ (Filing Date)
_____ (Application Number)	_____ (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
PCT/FR98/01513	10 July 1998	
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Steven B. Kelber, Reg. No. 30,073; Robert F. Gnuse, Reg. No. 27,295; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Martin M. Zoltick, Reg. No. 35,745; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Marc R. Labgold, Reg. No. 34,651; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,041; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Catherine B. Richardson, Reg. No. 39,007; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Sharon E. Crane, Reg. No. 36,113; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; and Paul E. Rauch, Reg. No. 38,591; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


1-00  
BRAVET, Jean-Louis  
NAME OF FIRST ~~SOLE~~ INVENTOR

X JL Bravet  
Signature of Inventor

X May 19, 1999  
Date

Residence: 5, avenue du Moulin  
F-60150 Thourotte  
FRANCE JRX  
Citizen of: FRANCE  
Post Office Address: same as above

200 MAURER, Marc  
NAME OF SECOND JOINT INVENTOR

  
Signature of Inventor

April 22, 1999  
Date

NAME OF THIRD JOINT INVENTOR

Signature of Inventor

Date

NAME OF FOURTH JOINT INVENTOR

Signature of Inventor

Date

NAME OF FIFTH JOINT INVENTOR

Signature of Inventor

Date

Residence: 7, rue Leon Debatisse,

B-4800 Verviers

BELGIUM

BEX

Citizen of: BELGIUM

Post Office Address: same as above

Residence:

Citizen of:

Post Office Address:

Residence:

Citizen of:

Post Office Address:

Residence:

Citizen of:

Post Office Address: